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Optical Spectroscopy of Copper (I) Doped- $\beta$ " Alumina<sup>Na<sup>+</sup></sup>

by

J.D. Barrie<sup>1</sup>, B. Dunn<sup>1</sup>, G. Hollingsworth<sup>2</sup> and J.I. Zink<sup>2</sup>

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1. Department of Materials Science and Engineering  
University of California, Los Angeles,  
Los Angeles, California 90024

2. Department of Chemistry and Biochemistry

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# OPTICAL SPECTROSCOPY OF COPPER (I) DOPED Na<sup>+</sup>-β"-ALUMINA

J.D. Barrie† and B. Dunn\*

Department of Materials Science and Engineering

University of California, Los Angeles, CA 90025

Gary Hollingsworth and Jeffrey I. Zink\*

Department of Chemistry and Biochemistry

University of California, Los Angeles, CA 90025



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## ABSTRACT

The luminescence spectra of Cu<sup>+</sup> doped Na<sup>+</sup>-β"-alumina single crystals reveal emission bands due to both Cu<sup>+</sup> monomers and Cu<sup>+</sup>-Cu<sup>+</sup> dimers. At low temperature, two monomer emissions (410nm and 440nm) and two dimer emissions (515 and 540nm) are observed. These bands are assigned to ions in specific sites within the β"-alumina conduction plane. The relative intensities of the emission bands are dependent on the sequence of irradiation and cooling. Changes in the relative intensities are caused by the photo-aggregation of the mobile Cu<sup>+</sup> ions to form dimers. These changes are an example of optical memory. The growth of the dimer emission band under ultraviolet excitation is a diffusion controlled process. The quenching of the monomer emission with increasing temperature correlates well with ionic hopping processes. The dynamics of ion motion which produce the green dimer emission band are quantified by a model based upon the thin film solution of Fick's second law.

† Current address: Materials Science Laboratory

The Aerospace Corporation, Los Angeles, CA 90009-2957

## INTRODUCTION

The ability of  $\beta''$ -alumina to incorporate a wide variety of ions within its structure has led to the synthesis of several isomorphs which possess interesting optical properties<sup>1,2</sup>. The  $\beta''$ -alumina structure is anisotropic and contains loosely packed two-dimensional "conduction planes" in which high cationic mobility is observed. This mobility enables the use of ion exchange reactions to introduce a large number of monovalent, divalent and trivalent cations into the  $\beta''$ -alumina structure. The conduction planes are separated by dense regions called spinel blocks which do not support ionic conductivity. Recent studies have shown the importance of optical spectroscopy as a means of probing the structural arrangements of luminescent species within the  $\beta''$ -alumina conduction plane<sup>3,4</sup>. In addition, studies have shown that the optical properties of some ions in  $\beta$  and  $\beta''$ -alumina are sensitive to the motion and arrangement of monovalent ions within the conduction plane<sup>5,6</sup>. The luminescent ions in these studies were stationary at the temperatures at which the spectra were recorded. Interesting photophysical and photochemical processes should arise when the optically active species themselves are mobile in the conduction plane.

Previously, we reported on the preparation and optical properties of  $\text{Cu}^+$  doped  $\beta''$ -aluminas. The unique ability to incorporate ions via ion exchange processes enabled us to produce single crystals with no trace of divalent copper. These  $\text{Cu}^+$  containing materials exhibited broadband emission, wavelength tunability, and single pass gain at room temperature<sup>7</sup>. The studies also suggested that the luminescence in these crystals was more complex than could be explained by the spectroscopy of isolated  $\text{Cu}^+$  ions within the  $\beta''$ -alumina host. In this paper, we present a more detailed study of the optical properties of  $\text{Cu}^+$  doped  $\text{Na}^+$ - $\beta''$ -alumina. The photoluminescence of the material is shown to arise from both  $\text{Cu}^+$  monomers and  $\text{Cu}^+$ - $\text{Cu}^+$  dimers. The mobility of the  $\text{Cu}^+$  ions is instrumental in the formation of the dimers. The

relative concentrations of the monomers and dimers and, thus, the intensities of the different emissions can be deliberately altered.

## EXPERIMENTAL PROCEDURES

Single crystals of  $\text{Cu}^+$  doped  $\text{Na}^+$ - $\beta$ "-alumina were prepared by standard ion exchange techniques<sup>7</sup>. The precursor crystals were grown by the flux evaporation technique<sup>8</sup> (nominal composition  $\text{Na}_{1.67}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17}$ ), and typically measured  $5 \times 5 \times 0.2 \text{ mm}$  in size. Crystals were immersed in molten salts containing 75 mole percent  $\text{CuCl}$  and 25 mole percent  $\text{NaCl}$  at temperatures from 400 to 600°C. Typical exchange times were two hours, but ranged from 15 min. to 12 hours. Flowing nitrogen was used during the exchange to prevent oxidation of the melt. The resultant exchanged crystals were colorless and single crystal x-ray diffraction measurements confirmed the retention of the  $\beta$ "-alumina phase. The c-axis lattice parameter of the exchanged crystals was typically  $33.54 \text{ \AA}$ , identical to the starting  $\text{Na}^+$ - $\beta$ "-alumina crystals. ESR measurements were unable to detect the presence of any divalent copper in these exchanged crystals. In addition, there was no indication that divalent copper species were formed (either transient or long-lived) when the crystal was subjected to ultraviolet irradiation during the ESR experiment.

The copper ion concentrations in the exchanged crystals were determined by chemical analysis (ICAP, Coors Laboratories) and by optical absorption techniques<sup>7</sup>. There was excellent agreement between these methods. In a typical crystal, the copper ion concentration was approximately  $5 \times 10^{18} \text{ ions/cm}^3$  (copper:sodium ratio 1:1000), although crystals with a range of concentrations were studied.

The excitation source for emission spectra was either an Argon ion laser for 351nm excitation or a XeCl excimer laser for 308nm excitation. For the low temperature (10K)

spectra, the sample was mounted on a copper block which was affixed to the cold tip of an AirProducts Displex closed cycle helium refrigerator. The emitted light was focussed onto the slit of a 1/3m monochromator (Jobin Yvon), dispersed across a diode array detector and the signal was processed with an optical multichannel analyzer (EG&G Model 1461). All spectra are uncorrected for wavelength response characteristics of the detector.

Emission and excitation spectra were obtained using a Spex F112A spectrofluorometer system equipped with a 150W Xenon arc lamp. Excitation spectra were corrected for the varying intensity of the lamp by using a Rhodamine B reference cell. Temperatures were varied from 77 to 300K using a fused quartz dewar.

Luminescent lifetimes of the crystals were measured using pulsed laser irradiation from a Lambda Physik XeCl excimer laser (nominal pulse duration 20 nsec). The luminescent signal was then discriminated using dielectric line filters centered at either 450nm or 540nm, and focussed onto a Hamamatsu R980 photomultiplier tube. The system response time was typically 2  $\mu$ sec, much shorter than any of the lifetimes measured. The signal was collected using either a Data Precision Model 6000 transient digitizer or a Tektronix 2230 digitizing oscilloscope, and was stored for analysis. The lifetimes were determined by a least squares regression fit of the slope of plots of the log of intensity versus time. The data showed single exponential behavior over at least three decades of intensity, enabling the lifetimes to be measured to accuracies of  $\pm 1\mu$ sec. Lifetimes were measured over a range of temperatures using the fused quartz dewar mentioned above.

## RESULTS

The emission spectrum of  $\text{Cu}^+$  ions in  $\text{Na}^+ \cdot \beta$ -alumina is comprised of several bands. The exact nature of the spectrum is strongly dependent on sample temperature and wavelength of excitation. Furthermore, the spectrum depends upon the thermal/optical history of the crystal.

The relative intensities of the bands can be deliberately changed by appropriate treatment of the crystals, but the band energies remain constant.

Samples of  $\text{Cu}^+$  doped  $\text{Na}^+-\beta''$ -alumina show a bright green luminescence centered at 535nm when excited with a variety of ultraviolet wavelengths at room temperature. When these samples are cooled to low temperatures, a broad blue luminescence is observed which consists of a distinct band at 440nm and a shoulder at 410nm. (The shoulder at 410nm appears as a distinct band in the spectrum of a sample which was irradiated during cooling - vide infra.) In addition, a green emission overlaps weaker bands to the red. This green band will be referred to as the 540nm band. The breadth of the bands and the overlap between them complicates determination of their exact positions. Figure 1 shows the emission spectra of a crystal at 10K and at 297K when excited at 351nm.

When the sample is excited at 308nm at 10K, a different emission spectrum is observed (figure 2). Again there are both blue and green emission peaks, but the blue emission no longer shows a distinct shoulder at 410nm, and the position of the green emission is shifted to 515nm.

The excitation spectra of the various emissions at 77K are shown in figure 3. The positions of the excitation bands for these peaks are given in Table 1. All four emissions show excitation bands around 300nm, suggesting the possibility of energy transfer. Energy transfer effects have been observed previously in several lanthanide ion exchanged  $\beta''$ -aluminas<sup>9</sup>. Only the emissions at 515 and 540nm show distinct excitation bands below 300nm.

The luminescent lifetimes for the blue and green emissions are also different. At 77K, the lifetime of the green emission at 540nm is 80 $\mu\text{sec}$ , while that of the blue emission at 440nm is 33 $\mu\text{sec}$ . Both emissions show a single exponential decay over several decades of intensity. Both the intensity and the lifetime of the blue emission decrease as the sample is heated above 77K. This trend continues until about 200K, where the intensity of the blue emission becomes negligible. In contrast, the intensity of the green emission increases as the temperature is

raised. The intensity reaches a maximum at approximately 430K. The lifetime varies only slightly over this temperature range (figure 4). The lifetimes observed for both the green and blue emissions are similar to the emission from triplet excited states of  $\text{Cu}^+$  in other hosts<sup>10</sup>.

The low temperature emission spectrum also depends upon the sequence of irradiation and cooling of the crystal. Figure 5a shows emission spectra for a crystal which had been cooled to 10K prior to the first application of the 351nm laser beam. As the sample was irradiated, the blue emission decreased in intensity while the green emission intensity significantly increased (Figure 5b). These changes occurred over a period of seconds and only in the part of the sample exposed to the irradiation. Lower power irradiation with the Xe lamp produced similar changes, but at a much slower rate. This shift in intensity from the blue to green was also observed when the samples were excited at 308nm using either the XeCl excimer laser or the Xe lamp. However, these changes were not observed when the excitation wavelength was changed to 240nm or greater than 400nm. Instead, the green emission gradually decreased with time.

## DISCUSSION

### 1. Peak Assignments

The emission bands in the  $\text{Cu}^+$  doped  $\text{Na}^+$   $\beta$ -alumina crystals arise from copper(I) monomers and dimers in a variety of sites in the conduction plane. The lifetimes and energies of the blue and green emissions demonstrate that they are from at least four distinctly different emitting species. The emission spectrum of the free  $\text{Cu}^+$  ion in the gas phase peaks at about 450nm<sup>11</sup>. The transition has been assigned as  $3d^9 4s \rightarrow 3d^{10}$ . The presence of a crystal field shifts the emission to higher energy by raising the energy of the 4s orbital with respect to that of the 3d orbitals<sup>12,13</sup>. The blue emission bands observed in  $\beta$ -alumina at 410nm and 440nm are at wavelengths similar to the emission of  $\text{Cu}^+$  in alkali halides<sup>14</sup>. Therefore, these two emissions are assigned to isolated  $\text{Cu}^+$  ions (monomers) in two different sites within the



$\beta''$ -alumina conduction plane.

The two possible sites for  $\text{Cu}^+$  ions in the conduction plane (figure 6) are the four-coordinated Beevers-Ross (BR) sites (which possess  $C_{3v}$  symmetry and are normally occupied by  $\text{Na}^+$  ions in the material) and the eight-coordinated mid-oxygen (mO) sites. The mO sites possess  $C_{2h}$  symmetry and are located directly between the oxygen ions in the conduction plane. The energy of the blue emission from  $\text{Cu}^+$  in alkali halide crystals depends upon the strength of the crystal field imposed by the host lattice. The emission peak is observed to shift to higher energies as the crystal field is increased. For example, when  $\text{Cu}^+$  substitutes for small ions such as  $\text{Li}^+$  in  $\text{LiCl}$ , the emission maximum is shifted to higher energies than that in  $\text{NaCl}$ <sup>12</sup>. These effects have been attributed to antibonding interactions of the  $\text{Cu}^+$  4s orbitals with the np orbitals of the surrounding ligands<sup>12,13</sup>. Previous studies<sup>15,16</sup> have shown that the mO site in  $\beta''$ -alumina is characterized by a slightly smaller crystal field than the BR site due to the longer ion-ligand distances for this site (2.81Å vs. 2.54Å). Based upon these results, the emission at 410nm is assigned to  $\text{Cu}^+$  monomers located in BR sites, and the emission at 440nm to monomers in mO sites. Because the luminescence quantum efficiencies for  $\text{Cu}^+$  ions in these two sites are likely to be different, it is not possible to determine the relative populations in these sites.

The two green emissions at 515nm and 540nm are assigned to  $\text{Cu}^+$ - $\text{Cu}^+$  pairs (dimers) in the conduction plane. Payne et al. observed similar emissions in  $\text{Cu}^+$  doped  $\text{SrCl}_2$  which were assigned to  $\text{Cu}^+$  pairs<sup>17</sup>. There are a number of ways to form pairs of  $\text{Cu}^+$  ions within the conduction plane of  $\beta''$ -alumina.  $\text{Cu}^+$  ions situated in adjacent BR sites would be within 3.2Å of each other, while  $\text{Cu}^+$  ions in adjacent mO sites would be separated by 2.6Å. In addition, structural studies of various ion exchanged  $\beta''$ -aluminas have shown that ions are frequently found to be off-center in these sites, further increasing the range of dimers which could be

formed<sup>18</sup>.

The spectra of the dimers can be explained by using the schematic energy level diagram for the  $\text{Cu}_2^{2+}$  dimer shown in figure 7. The diagram is based on the bonding between  $d^{10}$  valence shells which has been discussed by Hoffmann and others<sup>19-21</sup>. The 20 valence electrons of the dimer are accommodated in the molecular orbitals derived from the 10 d orbitals. The lowest unoccupied orbital is the  $\sigma$  bonding orbital derived from the two 4s orbitals. As the separation between the  $\text{Cu}^+$  ions is decreased, the overlap of the 4s orbitals is increased, pushing the  $\sigma$  bonding orbital closer to the  $\sigma^*$  antibonding orbital derived from the 3d atomic orbitals. Thus, shortening the  $\text{Cu}^+-\text{Cu}^+$  distance would produce a red shift of the emission spectrum. Based on these considerations, the emission at 540nm is assigned to the  $\text{Cu}_2^{2+}$  dimers spanning adjacent mO sites (2.6Å) and the emission at 515nm to  $\text{Cu}_2^{2+}$  dimers spanning adjacent BR sites (3.2Å). There is also the possibility of higher nuclearity clusters (trimers) or shorter  $\text{Cu}^+-\text{Cu}^+$  separations if the ions distort from the centers of the ideal sites. Evidence for the presence of these species is seen in the long wavelength tail of the emission spectrum of samples cooled to 10K before the first application of the excitation. These species are apparently unstable under ultraviolet irradiation. The red tail, visible only at such low temperatures, decreases in intensity with extended irradiation.

## 2. Effect of Ionic Motion on Optical Properties

### (a) Luminescence Quenching by Ionic Motion

$\text{Cu}^+$  doped  $\text{Na}^+-\beta$ -alumina represents a unique optical material in that the luminescent ion,  $\text{Cu}^+$ , is highly mobile within the structure. This ionic mobility leads directly to two spectroscopic features: quenching of the monomer emissions at temperatures above 200K and the dynamic changes observed in the spectra at low temperatures (figure 5). One item of

central importance in explaining these results is that the host material, Na<sup>+</sup>-β"-alumina, is a fast ion conducting solid. At room temperature, the observed Na<sup>+</sup> ion conductivity (10<sup>-1</sup> Ω<sup>-1</sup>cm<sup>-1</sup>)<sup>22</sup> is comparable to that of aqueous sodium chloride solutions. Using the Nernst-Einstein equation:

$$D = \frac{\sigma kT}{n(ze)^2} \quad (1)$$

(where D is the ionic diffusivity, σ is the ionic conductivity, and n and z the number and valence of the mobile ionic species) the observed conductivity can be related to ionic diffusivity. This diffusivity corresponds to the ionic jump frequency ω by the relation:

$$\omega = \frac{D}{fa_0^2N_v} \quad (2)$$

where f is the jump correlation factor, a<sub>0</sub> is the jump distance, and N<sub>v</sub> is the concentration of vacancies in the material. The observed conductivities translate into an ionic hopping rate of about 10<sup>9</sup> per second at room temperature. The Cu<sup>+</sup> ion is similar in size to Na<sup>+</sup> and has the same ionic charge. Thus, at low Cu<sup>+</sup> concentrations, the mobility of the Cu<sup>+</sup> ions in β"-alumina would be expected to be comparable to that of Na<sup>+</sup>.

Emission from Cu<sup>+</sup> monomers is observed at 77K when the hopping rate, ~4 sec<sup>-1</sup>, is substantially less than the radiative transition rate, ~10<sup>6</sup> sec<sup>-1</sup>. In this case, the copper monomer has a much higher probability of emitting a photon than hopping to an adjacent site. However, as the temperature increases, the hopping rate increases exponentially and monomer emission ceases. Thus, at room temperature, when the hopping rate is 10<sup>9</sup> sec<sup>-1</sup>, Cu<sup>+</sup> ions have a higher probability of deactivation by executing a hop than by emitting a photon. This quenching effect is novel for optical materials because traditional optical hosts are characterized by close packed structures, and ionic mobility in these materials is usually

negligible.

In contrast to the  $\text{Cu}^+$  monomer, the copper dimers are expected to be relatively immobile at room temperature and above. This reduced mobility is a result of the difficulty in moving larger and more highly charged species in the  $\beta''$ -alumina conduction plane. Previous work with divalent and trivalent cation exchange in  $\beta''$ -alumina clearly demonstrates this behavior<sup>23</sup>. With only one exception ( $\text{Pb}^{2+}$  in  $\beta''$ -alumina), the electrical resistivities for divalent and trivalent  $\beta''$ -alumina isomorphs are at least  $10^4$  times higher than  $\text{Na}^+$ - $\beta''$ -alumina over wide temperature ranges. Thus, the immobile copper dimers are luminescent at room temperature while the mobile copper monomers are susceptible to hopping deactivation.

Above 430K, both the luminescence intensity and lifetime of the dimer emission decrease rapidly, indicating that non-radiative processes begin to dominate. A possible mechanism of non-radiative decay is the thermal dissociation of the dimer bond<sup>19</sup>.

#### (b) Dimer Formation by Ionic Motion

The formation of the dimers and their increased stability under UV irradiation can be understood by reference to the energy level diagram of figure 7. There is only a slight net bond between the  $\text{Cu}^+$  ions in the ground state. Excitation to the lowest excited state of the dimer involves population of a bonding orbital and depopulation of an antibonding orbital. Therefore, the bonding between  $\text{Cu}^+$  ions is stronger in the excited state and the dimers are more stable under UV irradiation.

The formation of dimers and the increase of the dimer emission intensity with time of irradiation at low temperatures can also be explained by ion mobility. Evidence for this process was presented in figure 5, which shows that the emission spectrum is time dependent during ultraviolet irradiation at 10K. Attempts were made to quantify the growth of the green emission

peak under ultraviolet excitation. The growth of the dimer emission peaks was modelled assuming a simple thermally activated diffusion mechanism in which the diffusion source (isolated  $\text{Cu}^+$  ions) is gradually depleted. It was assumed that the distances between the  $\text{Cu}^+$  ions in the crystal followed a Gaussian distribution of the form:

$$P(x) = (\alpha/\pi^{1/2})\exp[-\alpha^2(x-x_0)^2], \quad (3)$$

where  $\alpha$  is a constant and  $x$  is the distance between  $\text{Cu}^+$  ions. The parameter  $x_0$  represents the mean distance between  $\text{Cu}^+$  ions. For the dopant levels studied,  $x_0$  was calculated to be on the order of  $50\text{\AA}$ . It was assumed that any excited  $\text{Cu}^+$  ion encountering any other  $\text{Cu}^+$  ion would form a fixed pair. The distances over which the  $\text{Cu}^+$  ions diffused were taken from the thin film solution of Fick's Second Law, which shows that the distance traveled by a diffusion front is proportional to  $(Dt)^{1/2}$ .<sup>24</sup> This solution assumes that the crystal size is much greater than the diffusion distances involved and is valid for  $\beta^*$ -alumina when the crystals are cooled to low temperatures. Thus the intensity of the dimer emission,  $I$ , was evaluated numerically as

$$I(t) \propto \sum_{t=t_0}^t P[(Dt)^{1/2}], \quad (4)$$

where  $P$  is the Gaussian function describing the profile of distances between isolated  $\text{Cu}^+$  ions. This function could be weighted by assuming that a portion of the  $\text{Cu}^+$  ions were already paired and had formed dimers prior to initial application of the ultraviolet irradiation. This was done by manipulation of the value used for  $t_0$  in equation (4). Figure 8 shows a plot of peak intensity versus time for the green (540nm) emission compared to the intensity calculated using equation (4). The observed time dependence of the spectra could be fit by assuming that the local temperature of the conduction plane was 24K higher than the 77K temperature of the crystals. In addition, it was assumed that one half of the  $\text{Cu}^+$  ions had formed pairs prior to the

experiment and that the range of distribution of the ions varied from 2.6Å (nearest neighbors) to 100Å. This was fixed by using a value of 0.067 for  $\alpha$ . The fit of the data to the above model for a diffusion controlled reaction with a finite source is shown to be quite good.

This result strongly indicates that the formation of the dimer species from the monomer is controlled by diffusion of  $\text{Cu}^+$  ions through the  $\beta''$ -alumina conduction plane. The fact that diffusion of these ions can be observed at low temperatures is remarkable. The activation energy for monovalent cationic conduction at these temperatures is expected to be of the order of 0.25eV, much greater than the thermal energy available (0.007eV at 77K, corresponding to jump frequencies of only  $\sim 4 \text{ sec}^{-1}$ ). Therefore the ultraviolet irradiation must provide the activation energy necessary for the ionic mobility which ultimately leads to dimerization. Thus the excitation wavelengths of 308nm and 351nm are not only absorbed by the ions, but also lead to phonon production which promotes ion transport and, eventually, dimer formation. The additional energy introduced via irradiation accounts for the observation that the jump frequency at 77K for  $\text{Cu}^+$  ions in the conduction plane is significantly higher under 351nm excitation ( $\sim 10^3 \text{ sec}^{-1}$  as determined from the above model) than occurs from just thermal energy ( $4 \text{ sec}^{-1}$  at 77K).

A very significant feature is that dimers do not form with 240nm excitation or with irradiation using wavelengths above 400nm. The excitation bands below 300nm are found only for the emission spectra attributed to  $\text{Cu}^+$  dimers, suggesting that these wavelengths excite the aggregate species directly. Since these wavelengths do not produce an increase in the green emission bands, it is likely that the photoaggregation process (i.e., dimerization) must be induced by excitation of the isolated  $\text{Cu}^+$  ions. Photoaggregation of metallic atoms in rare gas matrices<sup>25</sup> shows a similar wavelength dependence, with the dynamic processes occurring only at wavelengths absorbed by the mobile atoms.

The rate of formation of the  $\text{Cu}^+$  dimers under UV excitation was found to increase with

increasing temperatures, as is consistent with the diffusion mechanisms presented in this section. Unfortunately, it was not possible to measure the activation energy of the dimer formation process, since it was not possible to accurately determine the local temperature of the  $\text{Cu}^+$  containing planes during UV irradiation.

### 3. Optical Memory

The spectral and spatial selectivity of the 540nm emission constitutes the basis for the optical memory characteristics of  $\text{Cu}^+$  doped  $\text{Na}^+-\beta$ -alumina<sup>26</sup>. Optical writing can be achieved by focussing the laser on small regions of a crystal at low temperature. The changes in the luminescence occur only in the region of the crystal exposed to the radiation. Detection of the luminescence from the irradiated region corresponds to a read operation.

The changes are reversible. If the crystal is warmed to room temperature, the green emission is again observed uniformly throughout the crystal. Thus the memory can be erased and rewritten.

The optical memory depends on the mobility of the  $\text{Cu}^+$  ions in the conduction plane. Absorption of the incident radiation causes local heating and hence local mobility. If, in hopping to a vacant site, the mobile  $\text{Cu}^+$  ion encounters another  $\text{Cu}^+$  ion in an adjacent site, a dimer can be formed. Once formed, the dimer can subsequently be excited. Since the dimer is more stable in the excited state, it will remain paired. The result is an increase in the dimer concentration with extended irradiation, and an increase in the intensity of the green emission.

Dimers that are formed during the writing procedure stay together when the sample is left in the dark at low temperature. Samples have been held for hours in the dark after being cooled in the laser. When the laser excitation was resumed, the intensity of the dimer emission was the same as it had been before the excitation was interrupted.

## CONCLUSIONS

The high ionic mobility of  $\beta''$ -alumina gives rise to novel spectroscopic features including dynamic optical effects for  $\text{Cu}^+$  doped  $\text{Na}^+$ - $\beta''$ -alumina single crystals. The mobile luminescent ions are able to interact with each other and with the host lattice, and at least four emitting species can be observed under ultraviolet excitation. Low temperature optical spectroscopy has been used to determine the origin of the various emissions. The two blue emissions at 410nm and 440nm have been assigned to isolated  $\text{Cu}^+$  ions located in the BR and mO sites within the conduction plane. The two green emissions at 515nm and 540nm have been assigned to  $\text{Cu}^+$ - $\text{Cu}^+$  dimers situated in adjacent BR sites and adjacent mO sites, respectively. The excitation spectrum of the BR-BR dimer is similar to that of the excitation spectrum of the room temperature emission<sup>7</sup>, indicating that the emission from this dimer is predominant at room temperature.

The growth of the dimer emission bands under ultraviolet excitation is a diffusion controlled process and can be used to produce optical memory effects. The quenching of the monomer emission with increasing temperature correlates well with ionic hopping processes. The existence of dimer emission at room temperature and above is associated with the immobility of the dimer species and the enhanced bonding in the excited state.

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TABLE 1: Peak Positions for Excitation and Emission Bands

<u>Emission Peak</u>	<u>Excitation Peaks</u>
410	303, 342
440	302, 315
515	240, 280, 300
540	240, 280, 300, 355, 405

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#### FIGURE CAPTIONS:

- Figure 1 - Emission spectra for  $\text{Cu}^+$  doped  $\text{Na}^+-\beta''$ -alumina: top, 297K; middle, 10K, cooled in the dark; bottom, 10K, irradiated during cooling. The excitation wavelength is 351nm for all spectra.
- Figure 2 - Emission spectrum for  $\text{Cu}^+$  doped  $\text{Na}^+-\beta''$ -alumina at 10K with 308nm excitation.
- Figure 3 - Excitation spectra of several emission bands of  $\text{Cu}^+$  doped  $\text{Na}^+-\beta''$ -alumina at 77K. The emission wavelengths are as noted.
- Figure 4 - Lifetime and intensity of  $\text{Cu}^+$  doped  $\text{Na}^+-\beta''$ -alumina luminescence versus temperature in the region 80-540K. Lifetimes are indicated by  $\square$ , and intensity by  $\Delta$ .
- Figure 5 - Emission spectra of  $\text{Cu}^+$  doped  $\text{Na}^+-\beta''$ -alumina at 10K using 351nm irradiation. The crystal was cooled from 300K to 10K without excitation. (a) Initial spectrum. (b) Spectrum obtained after 30 seconds of laser irradiation.
- Figure 6 - View of the conduction plane of  $\text{Na}^+-\beta''$ -alumina. The large circles represent oxygen atoms above (open), below (shaded) and in (filled) the conduction plane. Sites 1 and 3 are the Beevers-Ross (BR) sites. Site 2 is the mid-oxygen (mO) site.
- Figure 7 - Schematic molecular orbital diagram depicting the interaction of two closed shell  $\text{Cu}^+$  ( $d^{10}$ ) ions. The dimer emission arises from the  $\sigma(4s) \rightarrow \sigma^*(3d)$  transition.
- Figure 8 - The emission intensity of  $\text{Cu}^+$  doped  $\text{Na}^+-\beta''$ -alumina at 545nm versus time during exposure of the crystal to 351nm irradiation at 77K. The solid line represents the calculated intensity determined from the diffusion model using an effective temperature of 101K.

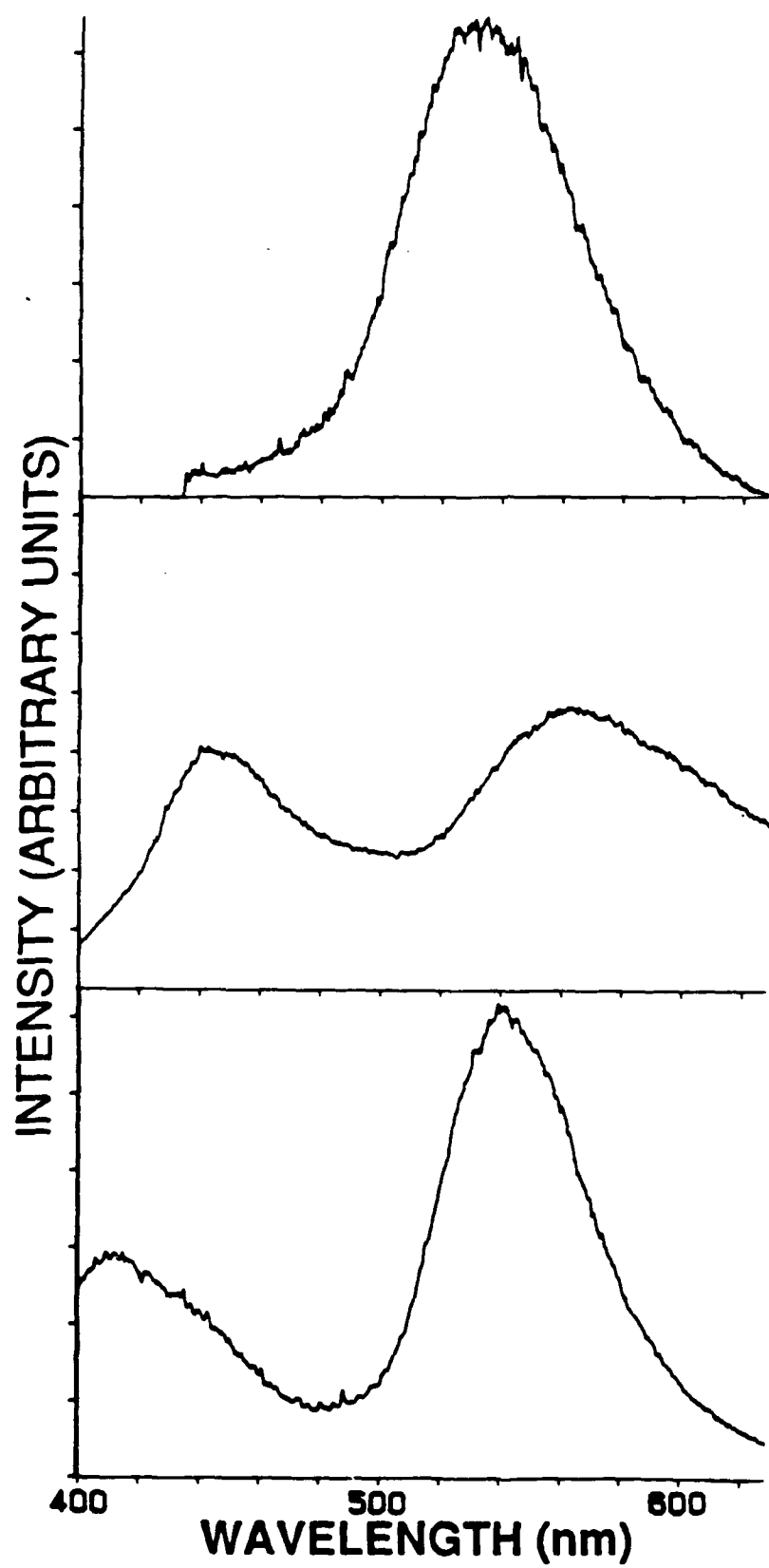


Fig 1

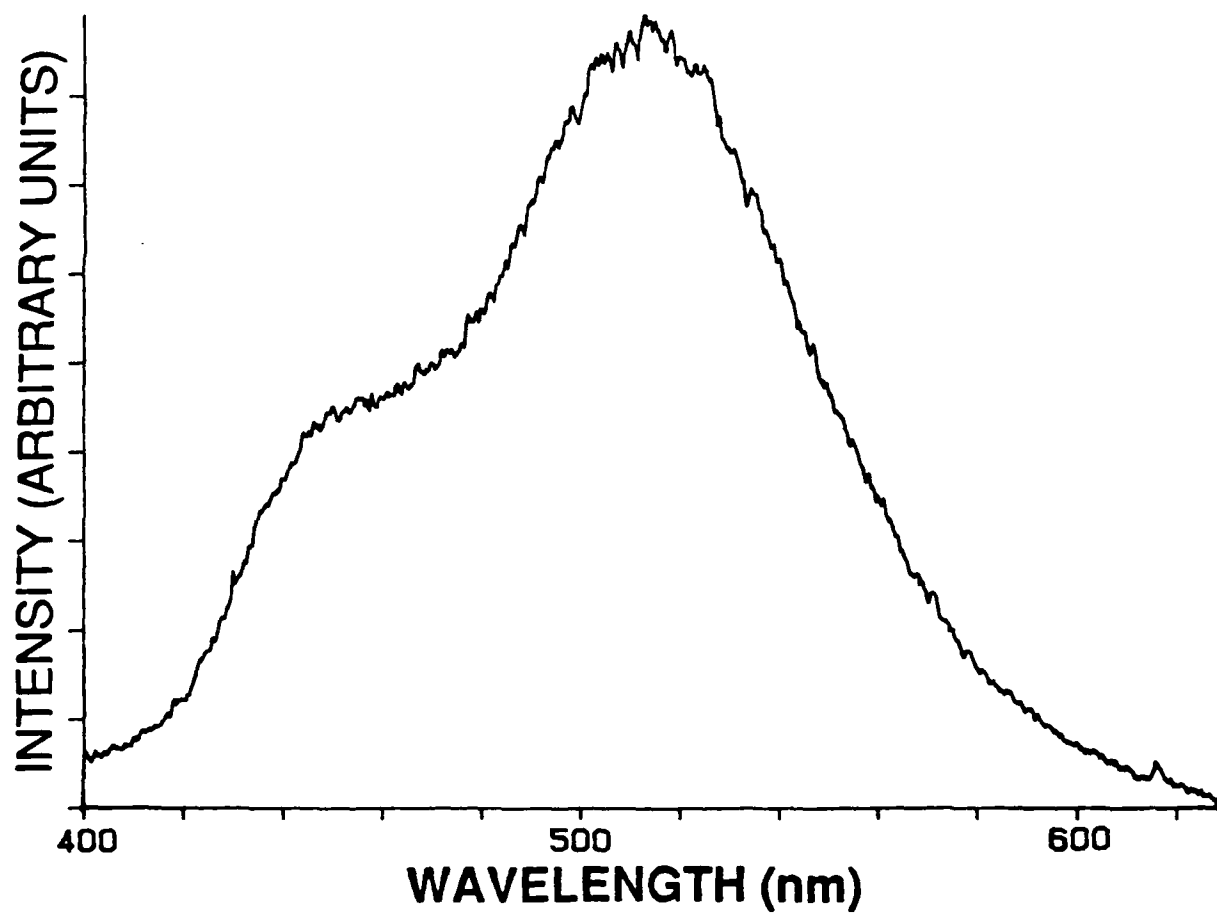


Fig. 2

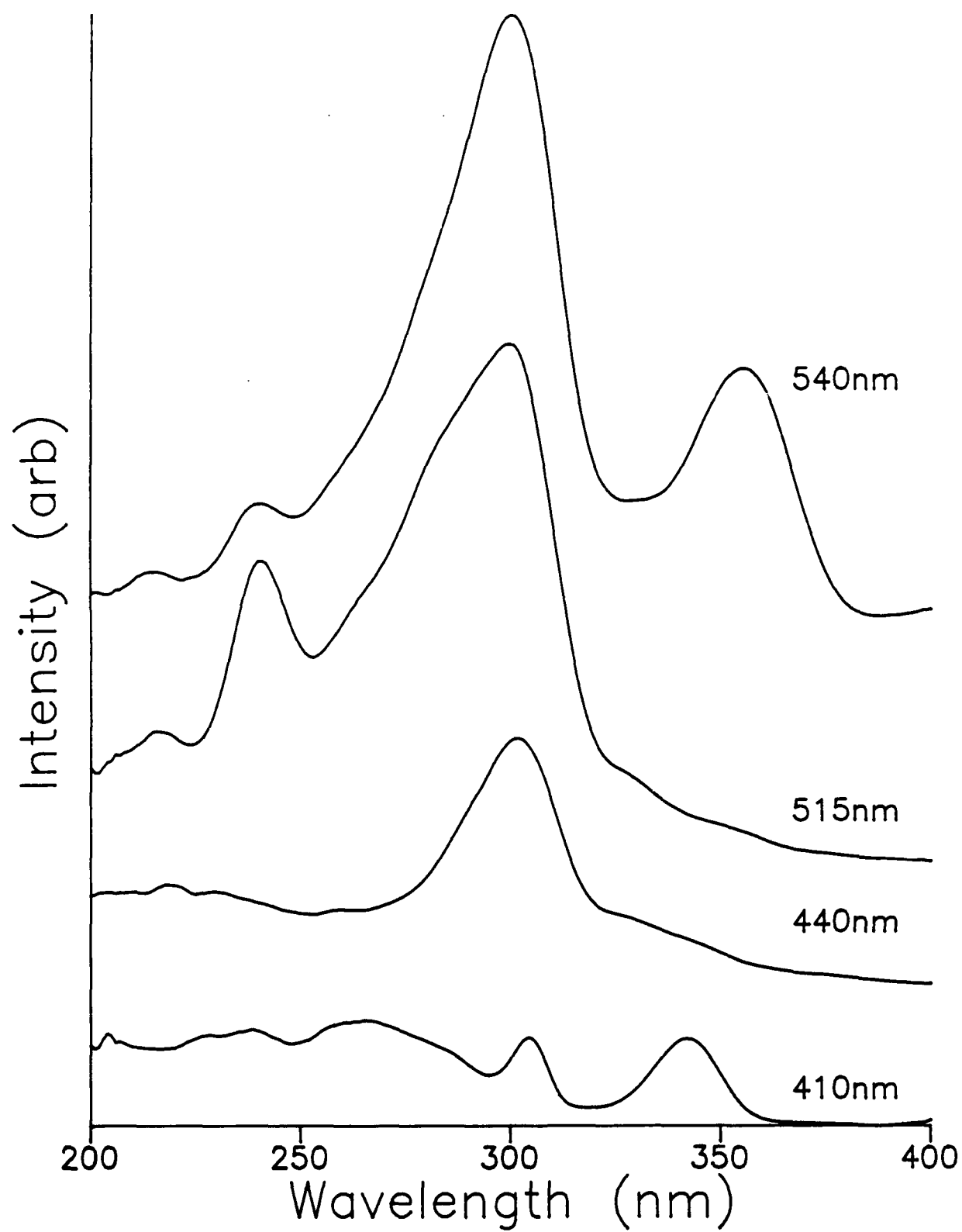
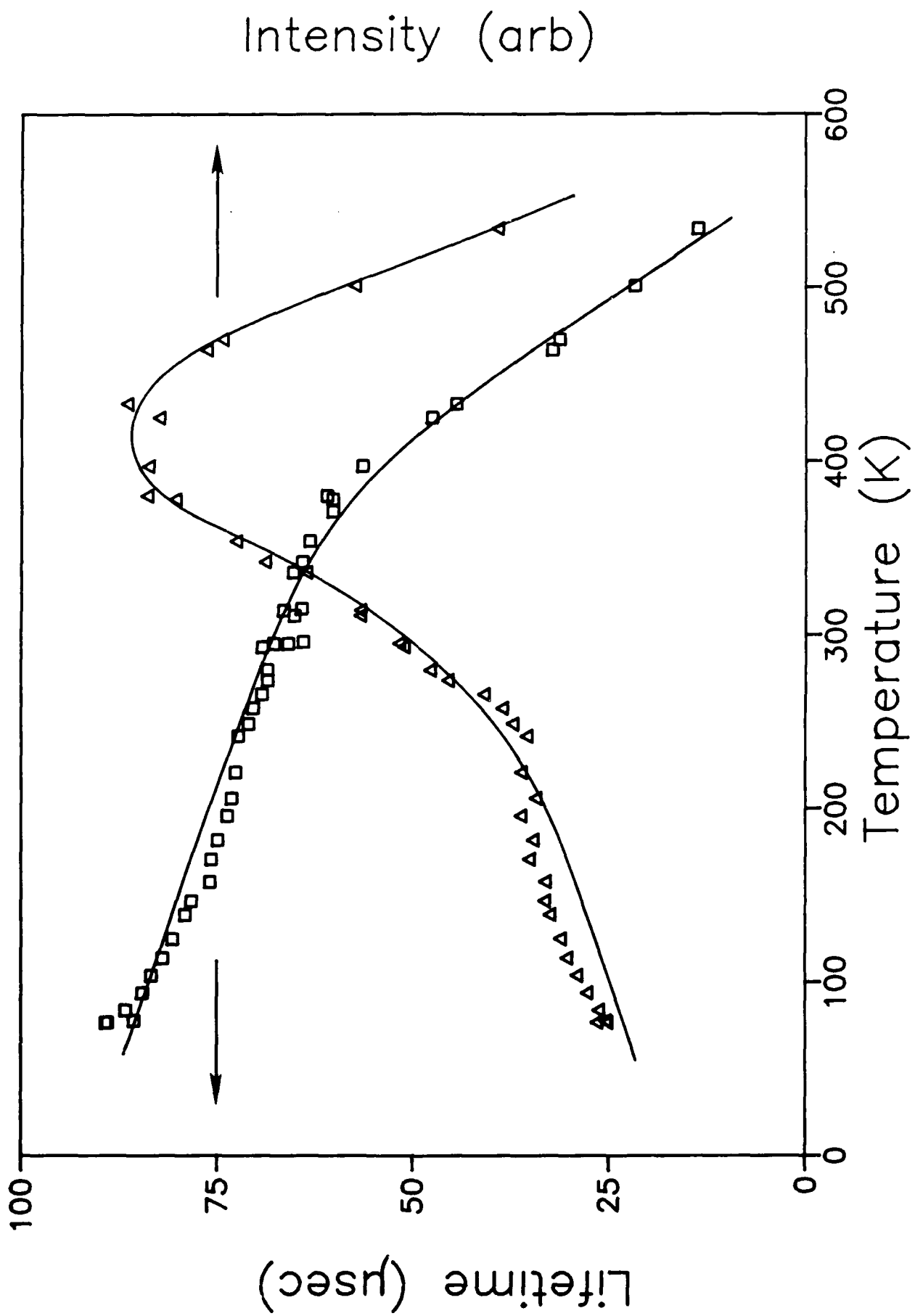


Fig. 3





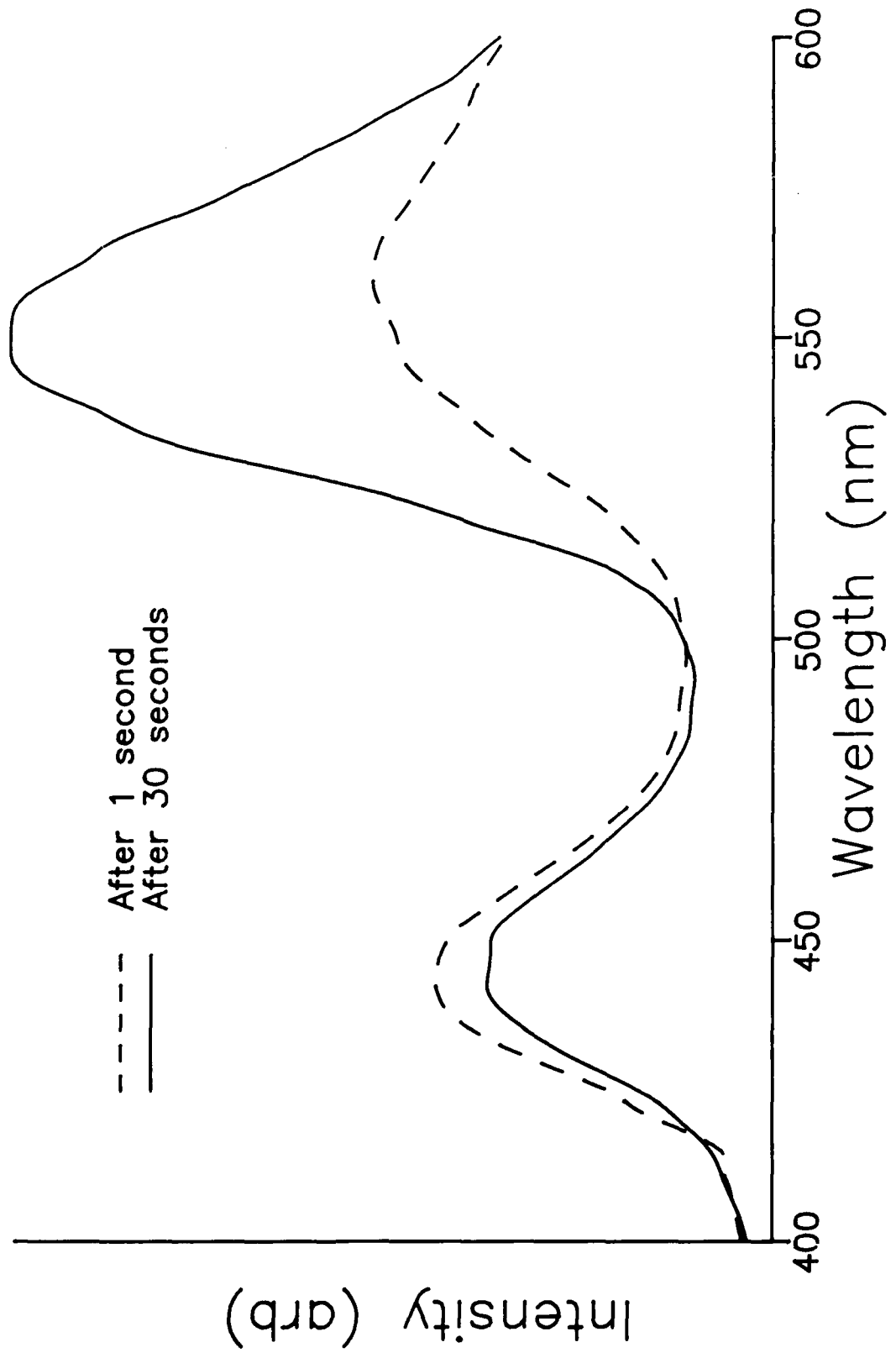
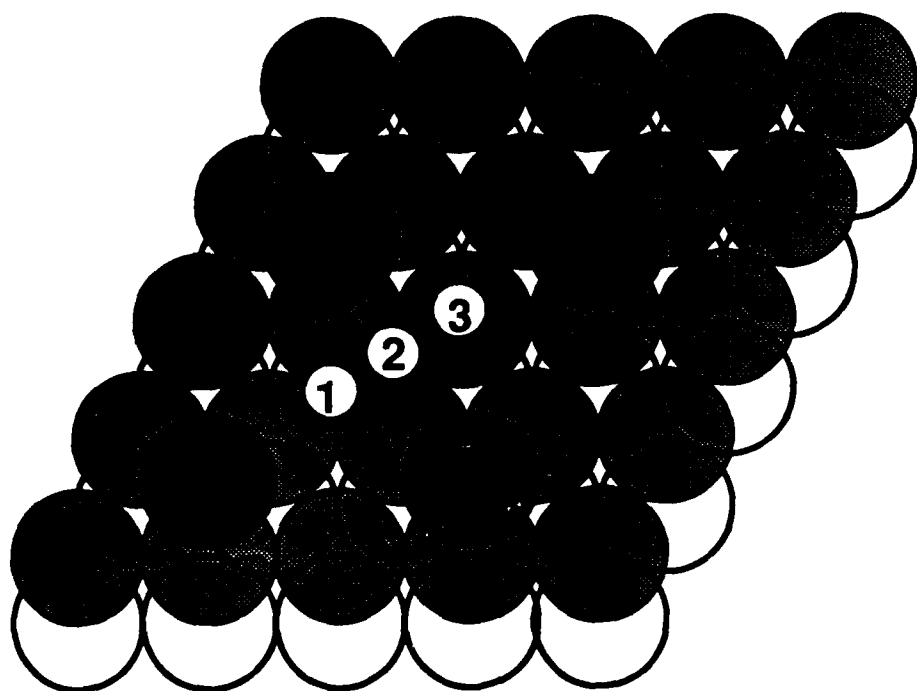


Fig 5



$\overline{\hspace{1.5cm}}$   
5.6 Å

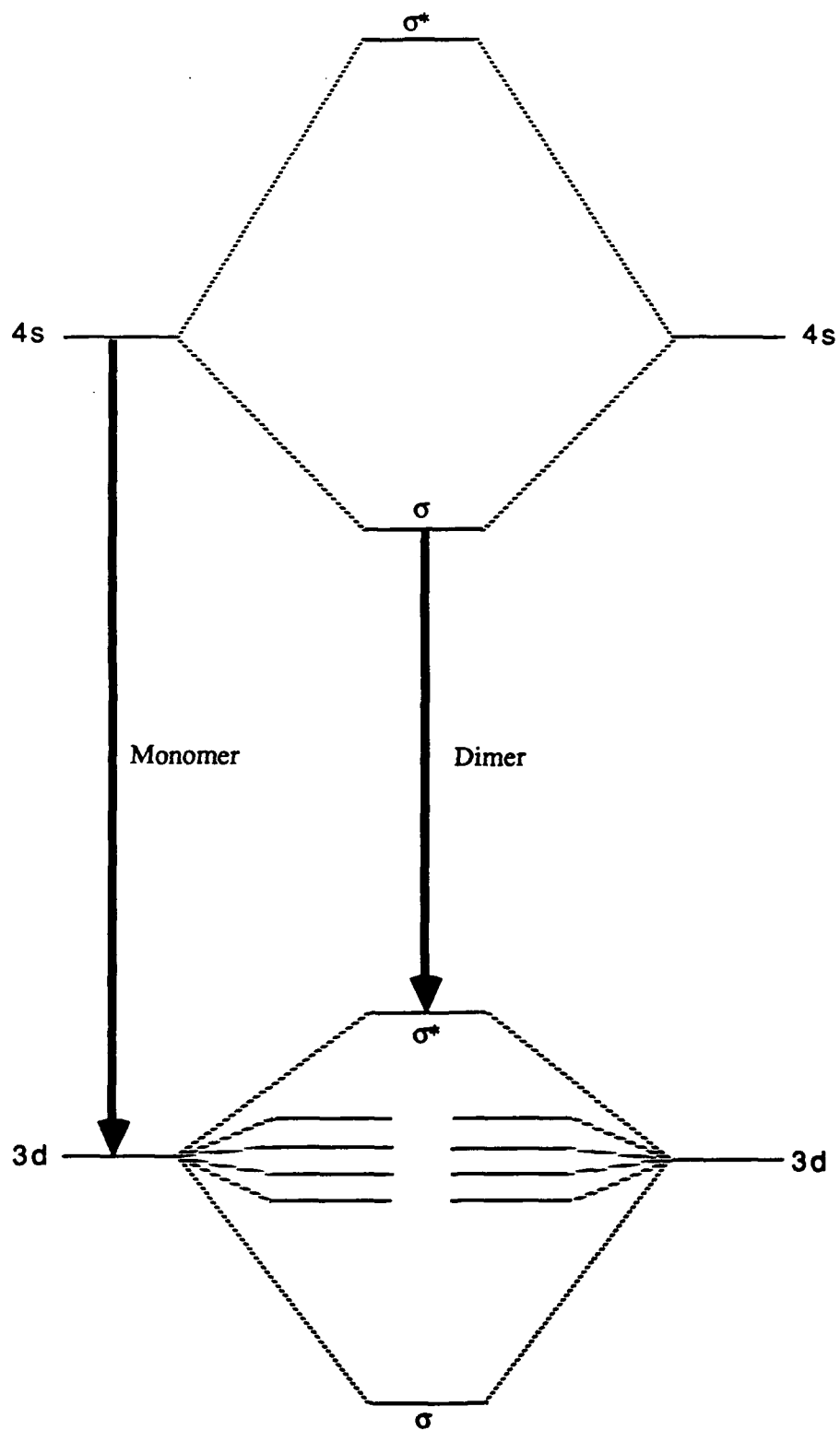


Fig. 7

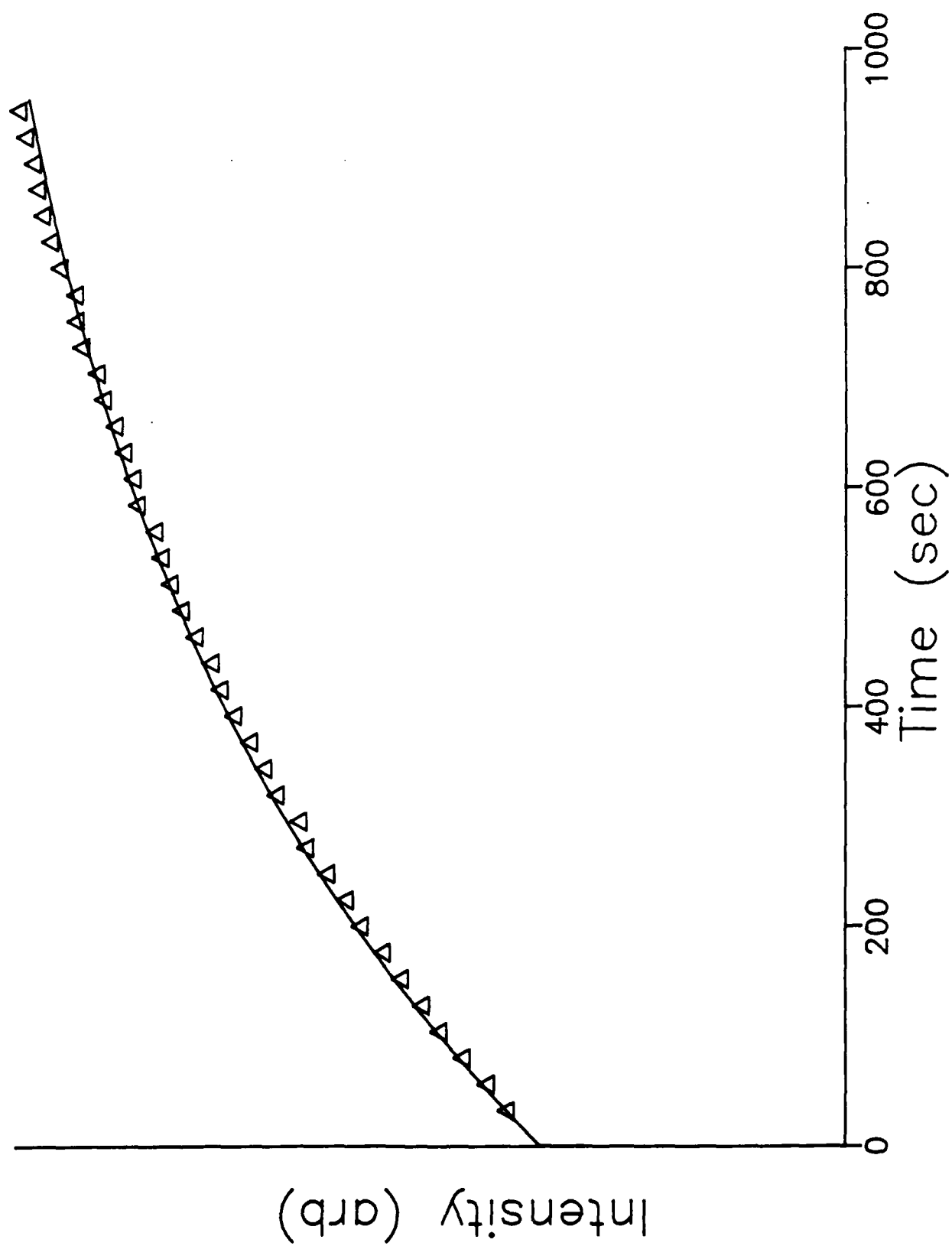


Fig 8